

## MODELING BIOMASS PYROLYSIS KINETICS AND MECHANISMS

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### ABSTRACT

Over the next decade there will be a renewed emphasis on the production of chemicals and liquid fuels from biomass, the use of agricultural wastes as feedstocks, and the co-firing of coal and biomass materials. In view of the tremendous diversity of biomass feedstocks, a great need exists for a robust, comprehensive model that could be utilized to predict the composition and properties of pyrolysis products as a function of feedstock characteristics and process conditions. The objective of this work is to adapt an existing coal pyrolysis model and make it suitable for the pyrolysis of biomass. The soundness of this approach is based on numerous similarities between biomass and coal. There are important differences, however, which preclude direct application of the coal model. This work involved: 1) selection of a set of materials representing the main types of biomass; 2) development of a biomass classification scheme; 3) development of a modeling approach based on modifications of a coal pyrolysis model; 4) calibration of the model for a set of standard materials against pyrolysis data taken over a range of heating rates; 5) validation of the model against pyrolysis data taken under other (higher) heating rate conditions.

### INTRODUCTION

The future outlook for biomass pyrolysis is quite promising, despite the fact that petroleum prices should remain low for at least the next decade [1]. The political and environmental benefits of using biomass will continue to provide impetus to the development of biomass pyrolysis processes (indigenous supply, low sulfur, no net CO<sub>2</sub>, biodegradable, etc.). The current level of activity is high (about 650 activities were identified in a recent study [2]), and international in scope. Over the next several years there will be a renewed emphasis on the production of chemicals from biomass with minimal upgrading, and on the use of agricultural wastes as feedstocks. Research and development activities will also continue on the production of liquid fuels and chemicals from biomass, and on the development of crops and farming techniques optimized for fuel or chemical production.

In view of the anticipated rapid development of pyrolysis-based processes, and because of the tremendous diversity of biomass feedstocks, a great need exists for a robust, comprehensive model that could be utilized to predict yields, composition and properties of pyrolysis products. Such a model would constitute a valuable tool in process development and scale-up. No such model is currently available. The specific problem addressed in this study was related to the inability to predict *a priori* gas, liquid, and solid products on the basis of known feedstock characteristics and process conditions (temperature, pressure, heating rate, residence time, etc.). This makes it difficult, of course, to design a process where the most desirable slate of products is produced. This, in turn, leads to appreciable, and often unnecessary, costs of product upgrading.

This work involved modifying the currently available FG-DVC coal devolatilization model [3,4], and making it suitable for modeling pyrolysis of agricultural and forestry feedstocks. The soundness of this approach was based on numerous similarities between biomass and coal, such as the fact that coal was formed from biomass, and that it can actually be viewed as petrified biomass. There are important differences, however, which preclude direct application of the coal model to pyrolysis of biomass, and which make it necessary to create a separate model dedicated to biomass conversion.

The FG-DVC model for coal pyrolysis combines a functional group (FG) model for gas evolution and a statistical depolymerization, vaporization, and cross-linking (DVC) model for tar and char formation [3,4]. The FG model currently predicts gas yields from the functional group sources in the coal using rank-dependent kinetics. The DVC model simulates coal as a macromolecular network and includes the processes of depolymerization, cross-linking, and transport. The model accurately predicts volatile yields, extract yields, cross-link densities, fluidity, and tar (oil) molecular weight distributions. The variations of the variables with pressure, devolatilization temperature, rank, and heating rate are also accurately reproduced.

A version of the FG-DVC model has been developed for lignin [5], which is similar to coal in being a cross-linked aromatic structure. However, in the case of whole biomass, the lignin component is a relatively minor constituent and the modeling approach must be adjusted to account for the dominant components (cellulose and hemicellulose).

### BACKGROUND

The pyrolysis of biomass has been the subject of numerous studies, as summarized in several reviews and collected papers [6-12]. Biomass pyrolysis is similar to coal pyrolysis with respect to pyrolysis products, which are char, tar and gases. Analogies are often drawn between pyrolysis of biomass and low-rank coals, but this should be done with caution. One of the principal differences is the fact that coal is predominantly an aromatic material, whereas the aromatic component of biomass (lignin) is a relatively minor constituent (~20%). In addition, because of the fossil nature

of coal, the mineral matter which has been incorporated into its structure influences the pyrolysis behavior in a different way than in the case of biomass. Biomass also has a much higher oxygen content as compared with coal. The oxygen is present as ether, hydroxyl, carboxyl, aldehyde, and ketone functionalities, which decompose during pyrolysis to produce oxygenated gases ( $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ). The yields of these species are similar to those produced by pyrolysis of low-rank coals (5–10 dry wt.% for  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , 5–15 dry wt.% for  $\text{CO}$ ). Biomass pyrolysis, however, produces much higher tar (liquid) yields as compared with low-rank coals (40–50% versus 10–20% on a dry basis). The increased tar yield comes primarily at the expense of char, the yield of which is much lower for biomass than for low-rank coals (<10% versus 40–50%). Apparently, the depolymerization of biomass is the predominant pyrolytic reaction, whereas, in the case of coal, depolymerization reactions compete with cross-linking events, which enhances char formation. Most of the char formed from biomass is derived from the lignin component, which is closest to low-rank coal in its chemical composition. As in the case of coal, the yield and distribution of products from pyrolysis of biomass depend on other variables in addition to the final temperature and holding time. These include heating rate, total pressure, ambient gas composition, and the presence of catalysts. An overview of these is given by Shafizadeh (in reference [10]). The trends are similar to those observed in coal, i.e., higher yields of volatiles are usually observed at higher heating rates, lower pressures, and in the presence of hydrogen. However, the data are quite scattered.

Historically, the quantitative modeling of biomass pyrolysis has proceeded along similar lines as for coal [1]. One approach is based on the approximation that the three main components of biomass (cellulose, hemicellulose, and lignin) behave independently during pyrolysis (see, e.g. Nunn *et al.* in ref. [10]). Consequently, yields can be predicted based on a knowledge of the pure component behavior. The shortcoming of this technique is that it cannot account for possible interactions between the biomass components. A more phenomenological approach was successfully used by Serio *et al.* [5] in modeling the pyrolysis of lignin. Their model was focused on observed evolution rates of major products rather than on the many individual reactions leading to the evolution of each product. The model of Serio *et al.* [5] and that of Petrocelli and Klein (discussed in reference [10]) involve a statistical treatment of lignin pyrolysis reactions. For the reasons discussed above, the network features of the FG-DVC model and similar models (such as the one proposed by Petrocelli and Klein) will be de-emphasized in favor of the original functional group (FG) description of gas and tar evolution [13,14]. While this is a more empirical approach, there is flexibility in the model to add more details of the whole biomass pyrolysis chemistry as these become known and can be represented in a tractable mathematical expression. A detailed review of modeling chemical and physical processes occurring during whole biomass pyrolysis can be found in reference [15]. Unlike in the case of coal, no comprehensive model of whole biomass pyrolysis has yet been developed.

## EXPERIMENTAL

**Sample Selection** - A number of biomass samples were first recommended based on the abundance and availability of agricultural and forestry feedstocks in the United States. The initial recommendations included softwood, hardwood, corn stalk, wheat straw, copy paper and newspaper. Cellulose, lignin, and hemicellulose were also recommended in order to individually study the three main components of biomass independently. This initial list was modified due to the limited ability to acquire standardized materials. Six samples were obtained from the National Institute of Standards and Technology's Standard Reference Materials Program which included microcrystalline cellulose (C), sugar cane bagasse (B), wheat straw (WS), corn stalk (CS), softwood *Pinus radiata* (PR), and hardwood *Populus deltoides* (PD). These six samples were supplemented with two samples of the pure component materials: lignin (L) and hemicellulose (HC). The identification and elemental composition of all nine samples is given in Table 1. To understand the chemical structure of these feedstocks, the starting materials were characterized by several methods including trace elemental analysis, ultimate analysis, proximate analysis, Field Ionization Mass Spectrometry (FIMS), solvent extraction and solvent swelling. This was complemented by a compilation of relevant literature data. FIMS and solvent extraction/swelling data will be reported in a separate publication.

**Ultimate and Proximate Analysis** - This work was done by Huffman Laboratories (Golden, Colorado). In addition, the samples were subjected to trace element analysis. Trace elements have often been implicated in influencing the pyrolysis behavior of whole biomass ([16]; also Shafizadeh in reference [10]).

**TG-FTIR Method** - Details of the TG-FTIR method can be found in references [17] and [18]. The apparatus, consists of a sample suspended from a balance in a gas stream within a furnace. As the sample is heated, the evolving volatile products are carried out of the furnace directly into a 5 cm diameter gas cell (heated to 150 °C) where the gases are analyzed by FT-IR spectroscopy. The FT-IR spectrometer obtains spectra to determine quantitatively the evolution rate and composition of several hydrocarbon compounds. Coal tars can also be quantified but biomass tars are appreciably different and for the lack of calibration data are determined from the mass balance. The system allows the sample to be heated on a pre-programmed temperature profile, at rates 3–100 °C min<sup>-1</sup>, up to a temperature between 20 °C and 1100 °C. Isothermal steps with a specified hold time are also possible.

## RESULTS AND DISCUSSIONS

**Biomass Classification Scheme** - The first step in modeling was to develop a classification scheme for whole biomass samples. Several researchers have taken the approach of modeling the pyrolysis of whole biomass using a linear superposition of the results for the three main components, i.e., cellulose, hemicellulose, and lignin ([19-21]; also Nunn *et al.* in reference [10]). However, a problem with this approach is that input information is not always known or easily obtained, and the amounts determined are not always consistent from one laboratory to another. In addition, Nunn *et al.* reported that modeling the evolution of individual species in high-heating-rate experiments was unsuccessful, although the modeling of the char yield produced good results [10]. The above scheme was also tested at Advanced Fuel Research (AFR) by trying to reproduce the TG-FTIR results for a whole biomass sample using a superposition of the TG-FTIR evolution profiles obtained for pure components. In general, this approach was unsuccessful for the evolution of individual species, and this is thought to be due to variations in the component compositions depending on their source, the effect of trace components on the pyrolysis behavior, and the problem in isolating unaltered pure components.

For this reason, it was decided that an alternative approach would be pursued, in which the samples are classified based on a van Krevelen diagram (plot of H/C versus O/C atomic ratios). A similar classification scheme has been successfully used for coal pyrolysis [22]. A plot of the six samples and the pure component samples are shown in Figure 1, along with literature results for other biomass samples. In general, the H/C ratio correlates with the O/C ratio, especially for the data collected at AFR. Variations in moisture content and errors in elemental analysis results are believed to be responsible for part of the scatter.

**Model Calibration** - The classification scheme lends itself to a linear interpolation of the total yields of pyrolysis products as well as the kinetic files based on the known elemental composition. However, since most of the whole biomass samples are closely clustered to either one of the woody (PD, PR) or herbaceous samples (CS, WS), it was decided to use a close-neighbor approximation. In this case, the input files are obtained from the nearest neighbor of the standard set of samples which were chosen to be L, CS, PD, and C. These samples were subjected to a more detailed characterization in order to calibrate the kinetic and composition files. In future work, some refinement of this scheme will be developed which allows for discrimination of small differences in composition.

The close-neighbor approximation is also confirmed by the TG-FTIR data as shown in Figures 2 and 3, where the evolution profiles for PR, PD, and B, and WS and CS are compared. The TG-FTIR data shows that PR, PD and B behave similarly, which is in agreement with the van Krevelen data from Figure 1. The same can be said about WS and CS. In addition, the following general observations concerning the TG-FTIR data can be made: (1) for each biomass sample, all gas-evolution peaks (except for methane) occur at approximately the same temperature; (2) the methane evolution peak of woody samples is bimodal, whereas only a single peak is present in the case of herbaceous biomass; (3) all the herbaceous-samples peaks occur at temperatures approximately 30 °C lower than the corresponding peaks for the woody samples; and (4) a small low-temperature peak can be seen in the evolution patterns of the herbaceous samples.

**Kinetics and Yields Determination** - In what follows, the determination of the kinetic parameters and total yields of individual species is described in some detail. In general, the approach is similar to that applied to coal, i.e., the evolution of each functional group is described by a first-order reaction with a distributed activation energy of width  $\sigma$  [4]. In the case of biomass pyrolysis, a smaller number of functional groups is required to describe the process as the evolution of each species can usually be represented by the decomposition of a single functional group. In other words, each gas species released during biomass pyrolysis evolves in the form of a single peak, which is in contrast to coal pyrolysis where several peaks can be observed for an individual species. Methane is an exception, in the sense that it requires two functional groups in the case of coals and woody biomass, but only a single peak for herbaceous biomass.

Since the TG-FTIR biomass data show that, for each sample, the tar and other gas species evolve at the same temperature (Figs. 2 and 3), the same value of the activation energy was used for all species. This activation energy was derived from the overall weight-loss curve, and a non-isothermal  $T_{max}$  method was used for this purpose [23].  $T_{max}$  is the temperature at which the rate of volatile evolution is maximum. Typically,  $T_{max}$  is measured at several heating rates, and the activation energy  $E$  and the pre-exponential factor  $A$  can be extracted from the equation:  $\ln(M/T_{max}^2) = \ln(A/E) - E/(RT_{max})$  [23].

Although the value of  $E$  was kept identical for the biomass tar and all the gas species, slight adjustments in the value of  $\sigma$  were performed in order to match more closely the width of the evolution peak of each species. The amounts of the functional groups, and the corresponding yields of the volatiles, were obtained by fitting the model to the TG-FTIR data. The results from this analysis are given in Table 2. The values for the activation energies obtained are consistent with previous literature results [24]. The apparent discrepancy between our kinetic parameters and those reported for cellulose by Antal and Varhegyi [25] can be explained by the differences in the processing of raw experimental data. A detailed discussion of this topic will be included in a future publication.

**Model Validation** - Model predictions were compared with the yields and composition of pyrolysis products obtained under different conditions from those used to determine model

parameters (e.g., different heating rates). An example is shown in Fig. 4 for the high heating rate data of Nunn *et al.* (1000 K/sec) [26]. Experimental data for sweet gum hardwood are compared with model predictions generated using the kinetic input files for PD. The results are reasonable for the overall weight loss (Fig. 4) and CO<sub>2</sub> (not shown), but they are less good for the other gas species. In addition to the simplifications inherent in the predictive model, and the differences in the composition of the two materials, the observed discrepancies could also result from uncertainties in the time-temperature history and/or secondary reactions which alter the product distribution. Future work will involve refinement of the model to include secondary reactions, mineral effects, heating-rate effects, and an improved classification scheme to account for composition differences.

## CONCLUSIONS

The FG-DVC coal pyrolysis model has been successfully applied to biomass. Preliminary data show that it may be possible to model the pyrolysis behavior of different biomass feedstocks using kinetic parameters and product yields interpolated among selected data-base materials (standards). The linear interpolation scheme is based on the feedstock elemental composition. Refinements of the proposed scheme and further validation of the model are under way.

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## REFERENCES

- 1 Serio, M. A., Wójtowicz, M. A. and Charpenay, S., "Pyrolysis," *Encyclopedia of Energy Technology and the Environment* (A. Bisio and S. G. Boots, Eds.), John Wiley & Sons, New York, 1995.
- 2 Bridgwater, A. V., *Biomass*, **22** (1-4), 279 (1990).
- 3 Solomon, P. R., Hamblen, D. G., Carangelo, R. M., Serio, M. A., and Deshpande, G. V., *Combustion and Flame*, **1988**, **71**, 137.
- 4 Solomon, P. R., Hamblen, D. G., Serio, M. A., Yu, Z. Z., and Charpenay, S., "A Characterization Method & Model for Predicting Coal Conversion Behavior," *Fuel*, **72**, (4), 489 (1993).
- 5 Serio, M. A., Charpenay, S., Bassilakis, R., and Solomon, P. R., "Measurement and Modeling of Lignin Pyrolysis", *Journal of Biomass & Bioenergy*, Vol. 7, Nos. 1-6, 107 (1994)
- 6 Antal, M. J., Jr., in *Adv. in Solar Energy* (Boer, K. W., Duffie, J. W., Eds.), American Solar Energy Society, Boulder, CO, **1**, 61 (1984); **2**, 175 (1985)
- 7 Shafizadeh, F., in *Proc. Specialists' Workshop on Fast Pyrolysis of Biomass* (J. Diebold, Ed.), SERI/CP-622-1096, Solar Energy Research Institute, Golden, CO, 79 (1980)
- 8 Shafizadeh, F., in *The Chemistry of Solid Wood* (R. M. Rowell, Ed.), *Advances in Chemistry Series No. 207*, American Chemical Society, Washington, DC (1984).
- 9 Bridgwater, A. V., and Cottam, M.-L., *Energy and Fuels*, **6**, (2), 113 (1992)
- 10 Overend, R. P., Milne, T. A., and Mudge, L. K., Eds., *Fundamentals of Thermochemical Biomass Conversion*, Elsevier, (1985)
- 11 Soltes, E. J., and Milne, T. A., Eds., *Pyrolysis Oils from Biomass: Producing, Analyzing and Upgrading*, ACS Symposium Series No. 376, American Chemical Society, Washington, DC (1988)
- 12 Chum, H. L., and Powers, A. J., in *Emerging Technologies for Materials and Chemicals from Biomass* (R. M. Rowell, T. P. Schultz, and R. Narayan, Eds.), ACS Symposium Series No. 476, ACS, Washington, DC, pp. 339-353 (1993).
- 13 Solomon, P. R. and Hamblen, D. G., Ch. 5 in *Chemistry of Coal Conversion* (R. H. Schlosberg, Ed.), Plenum, New York, 1985, pp. 121-251.
- 14 Serio, M. A., Hamblen, D. G., Markham, J. R. and Solomon, P. R., *Energy & Fuels*, **1**, 138 (1987).
- 15 Di Blasi, C., *Prog. Energy Combust. Sci.*, **19**, 71 (1993).
- 16 Varhegyi, G., Antal, M. J., Jr., Szekeley, T., Till, F., Jakab, E. and Szabo, P., *Energy & Fuels*, **2**, 273 (1988).
- 17 Carangelo, R. M., Solomon, P. R. and Gerson, D. J., *Fuel*, **66**, 960 (1987).
- 18 Whelan, J. K., Solomon, P. R., Deshpande, G. V., Carangelo, R. M., *Energy and Fuels*, **2**, 65, (1988)
- 19 Koufopoulos, C. A., Maschio, G. and Lucchesi, A., *Can. J. Chem. Eng.*, **67**, 75 (1989).
- 20 Ward, S. M. and Breslaw, J., *Comb. Flame*, **61**, 261 (1985).
- 21 Miller, R. S. and Bellan, J., submitted to *Combust. Sci. Tech.* (1996).
- 22 Zhao, Y., Serio, M. A., Bassilakis, R. and Solomon, P. R., *Twenty-Fifth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, 1994, pp. 553-560.
- 23 Van Heek, K. H. and Juentgen, H., *Ber. Bunsenges. Phys. Chem.*, **72**, 1223 (1968).

- 24 Milosavljevic, I. and Suuberg, E. M., *Ind. Eng. Chem. Res.*, **34**, 1081 (1995).  
 25 Antal, M. J., Jr. and Varhegyi, G., *Ind. Eng. Chem. Res.*, **34**, 703 (1995).  
 26 Nunn, T. R., Howard, J. B., Longwell, J. P. and Peters, W. A., *Ind. Eng. Chem. Process Des. Dev.*, **24**, 836 (1985).

**Table 1.** Proximate, ultimate, and trace-element analyses of the biomass samples used in this study (wt.%). Dry loss is on an as-received basis, while all other results are reported on a dried-sample basis. Legend: CS = Corn Stalk; WS = Wheat Straw; B = Sugar Cane Bagasse; PR = *Pinus radiata*; PD = *Populus deltoides*; C = Cellulose; ALC = ALC Lignin

	CS	WS	B	PR	PD	C	ALC
Dry Loss	5.0	7.9	7.1	6.6	6.6	4.8	N/A
Carbon	45.6	43.7	47.3	49.9	49.1	44.0	67.4
Hydrogen	5.9	5.6	5.8	6.1	6.0	6.4	6.2
Oxygen	44.0	40.9	42.8	43.6	43.8	49.5	26.3
Nitrogen	0.72	0.62	0.17	0.05	0.09	0.03	0.20
Sulfur	0.10	0.19	0.04	0.02	0.06	< 0.01	N/A
Ash	3.8	9.0	3.9	0.25	0.91	< 0.05	< 0.05
Vol. Matter	89.8	72.8	79.3	82.8	83.5	92.7	N/A
Fixed Carbon	6.4	18.2	16.8	17.0	15.6	7.3	N/A
Al	N/A	N/A	0.2%	L	L	N/A	N/A
Si	N/A	N/A	0.3%	L	L	N/A	N/A
Na	N/A	N/A	L	L	L	N/A	N/A
K	N/A	N/A	0.03%	0.02	0.02%	N/A	N/A
Fe	N/A	N/A	0.1%	N	N	N/A	N/A
Mg	N/A	N/A	L	N	N	N/A	N/A
Ca	N/A	N/A	0.05%	L	0.1	N/A	N/A
Ti	N/A	N/A	0.05%	N	N	N/A	N/A
Mn	N/A	N/A	50 ppm	N	N	N/A	N/A
B	N/A	N/A	L	N	N	N/A	N/A
Ba	N/A	N/A	L	N	N	N/A	N/A
Be	N/A	N/A	L	N	N	N/A	N/A
Cr	N/A	N/A	L	N	N	N/A	N/A
Ni	N/A	N/A	L	N	N	N/A	N/A
V	N/A	N/A	10 ppm	N	N	N/A	N/A

L = Detected but below detection limit, N = Not detected, N/A = Not Available

**Table 2.** Kinetic parameters and yields for the pyrolysis of corn stalk and *Populus deltoides*.

Sample	Species	A (s <sup>-1</sup> )	E/R (K)	σ/R (K)	Yield (wt.% daf)
Corn Stalk	CO <sub>2</sub>	$8.3 \times 10^{13}$	22500	700	5.1
	CO	$8.3 \times 10^{13}$	22500	700	2.2
	H <sub>2</sub> O	$8.3 \times 10^{13}$	22500	700	7.4
	CH <sub>4</sub> Tight	N/A	N/A	N/A	N/A
	CH <sub>4</sub> Loose	$5.2 \times 10^{12}$	27500	2000	0.8
	Tar	$8.3 \times 10^{13}$	22500	100	63.5
Populus Deltoides	CO <sub>2</sub>	$2.8 \times 10^9$	17000	700	5.2
	CO	$2.8 \times 10^9$	17000	700	3.4
	H <sub>2</sub> O	$2.8 \times 10^9$	17000	700	10.4
	CH <sub>4</sub> Tight	$6.0 \times 10^{13}$	31000	2500	0.54
	CH <sub>4</sub> Loose	$3.0 \times 10^{13}$	25000	1500	0.36
	Tar	$2.8 \times 10^9$	17000	100	55.2

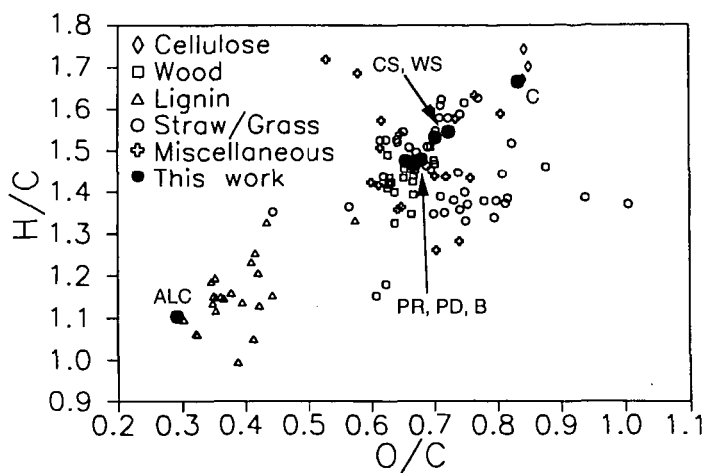


Figure 1. The van Krevelen diagram for biomass samples. H/C and O/C are atomic hydrogen-to-carbon and oxygen-to-carbon ratios.

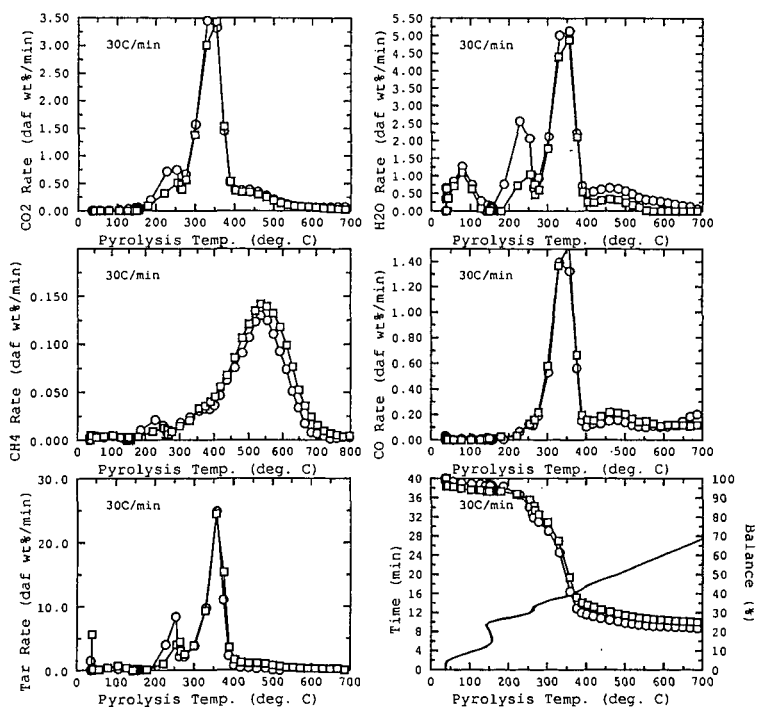


Figure 2. The TG-FTIR data for two herbaceous samples: corn stalk (circles) and wheat straw (squares).

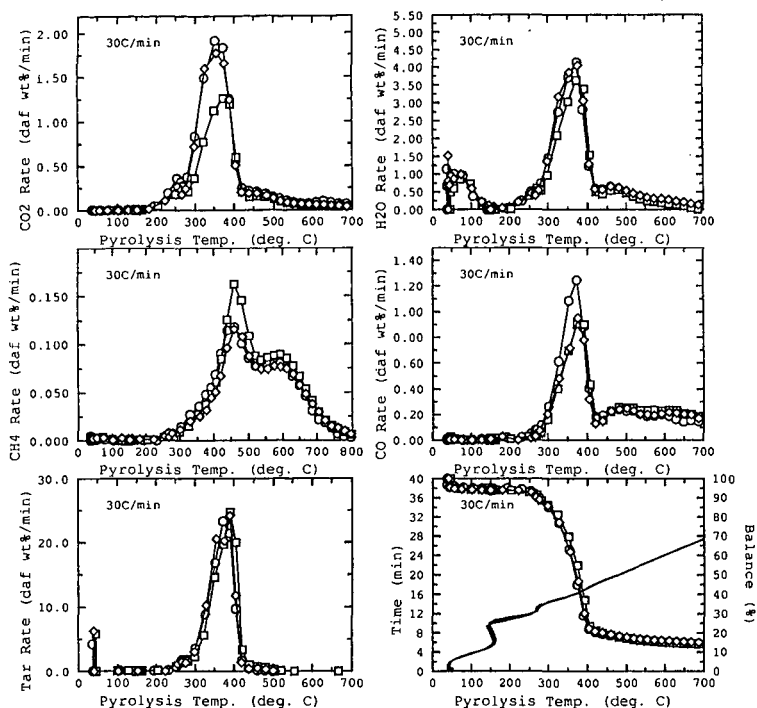


Figure 3. The TG-FTIR data for two woody samples: *Populus deltoides* (circles) and *Pinus radiata* (squares). The position of sugar cane bagasse on the van Krevelen diagram is in close proximity to the above two samples, and the TG-FTIR data for bagasse (diamonds) exhibit gas-evolution patterns similar to those of *Populus deltoides* and *Pinus radiata*.

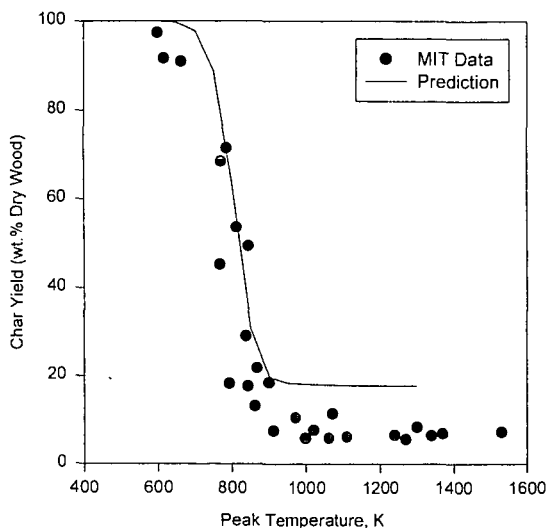


Figure 4. The comparison of char-yield experimental data (Nunn *et al.* [26]) and model predictions using the kinetic input files and product yields for *Populus deltoides*. The heating rate is 1000 K/s.